

Colloidal stability of sulfonated polystyrene model colloids. Correlation with electrokinetic data

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Abstract. In this work we describe the colloid stability of functionalized latexes: two sulfonated polystyrene model colloids with the same particle size and different surface charge densities. The critical coagulation concentration (ccc) was determined in the presence of two electrolytes (1:1 and 2:2), being around 0.75 M and 0.075 M, respectively. By the DLVO theory the electrokinetic and colloid stability data were correlated to calculate the Hamaker constant at both experimental conditions. By comparing the experimental and theoretical values of the Hamaker constant, it is possible to get more information about the colloidal stabilization mechanism of functionalized latexes. In the case of sulfonated latexes, the electrostatic and steric contributions occur, with different influence for each latex depending of their surface electric charge.

Key words: Sulfonated polystyrene latexes – colloid stability

Introduction

Monodisperse spherical polystyrene latexes have proven to be model systems which are widely used in many practical applications and are also suitable for studying fundamental colloidal phenomena. Recently, papers have appeared [1–3] describing the preparation of sulfonated polystyrene latexes with independent control of the particle size and surface charge density. The sulfonated functionality was selected because of its stability against hydrolysis. Due to the difficulty of independent control of the particle size and surface functional group densities, the effect of surface charge density on colloidal stability has been scarcely studied [4].

In previous papers [5–7] the electrokinetic characterization of highly sulfonated polystyrene particles with similar particle size and different surface charge densities was accomplished. In these papers the effect on the electrophoretic mobility of an extensive and systematic cleaning process, and the addition of different electrolytes were studied [5, 6]. The zeta-potentials were also estimated by using several theories, one including

the correction due to the anomalous surface conductance [7].

The objective of this work is to continue with the characterization of sulfonated polystyrene latexes by studying their colloidal stability. The stability factor and the critical coagulation concentration (ccc) were studied for two sulfonated polystyrene latexes with the same particle size and different surface charge densities. Two symmetrical electrolytes, magnesium sulfate (2:2) and potassium bromide (1:1), were used for this study. These results were correlated with the electrokinetic data by means of the DLVO theory. In this way the Hamaker constant was estimated and compared with the theoretical value.

Experimental

Materials

Two sulfonated polystyrene latexes prepared by “shot-growth” emulsion polymerization were used throughout this work. The preparation, cleaning process and surface characterization of

Table 1. Particle size, polydispersity index, and surface charge density of sulfonated polystyrene latexes, and amount of NaSS added at the second injection.

Latex	Nass (g) 2 nd injec.	Dn (nm)	Stand. Deviat. (nm)	Dw (nm)	PDI	σ_0 $\mu\text{C}/\text{cm}^2$
SN-8	1.2	179	6	179	1.003	12.3
SN-13	1.6	178	8	179	1.007	17.0

those latexes were described in a previous paper [6]. As a summary, Table 1 shows the particle size, polydispersity index, surface charge density and the amount of sodium styrene sulfonate (NaSS) added at the shot injection, for both latexes.

The coagulating electrolytes, magnesium sulfate and potassium bromide, were reagent grade and were used as received without further purification. Double-distilled and deionized (DDI) water was used throughout.

Measurement of stability ratios

In a typical coagulation experiment, 2.4 ml of the latex dispersion, with a number of 10^{10} particles per ml, were put into the cell. 0.6 ml of a giving electrolyte solution were added and mixed. The device used for the rapid addition and mixing of electrolyte to the suspension for the study of coagulation kinetics was described in ref. [8]. The time variation of the turbidity upon addition of electrolyte was followed in a Spectronic 601 (Milton Roy, USA) spectrometer at a wavelength of 420 nm. The spectrometer is connected to a personal computer, which collects the data and calculates the initial slopes of the turbidity curves.

From the ratios of the initial slopes of the slow coagulation runs to that of the fast coagulation runs, the stability factor values (W) for each electrolyte concentration were calculated [9].

Results and discussion

As Reerink and Overbeek have shown [10], with several approximations, a linear relationship between $\log W$ and $\log C$, could be obtained:

$$\log W = -k' \log C + \log k'' \quad (1)$$

where k' and k'' are constants and C is the electrolyte concentration. Thus, W decreases with the addition of electrolyte until the electrolyte concentration reaches a critical value above which the energy barrier between particles disappears. The electrolyte concentration at which W becomes equal to 1 is called the critical coagulation concentration (ccc). The ccc is defined as the concentration of added electrolyte just sufficient to bring about diffusion-controlled, rapid coagulation [11].

Low W values have been plotted versus $\log C$ as suggested by Reerink and Overbeek [10]. Figure 1 shows the stability curves of latexes SN-8 and SN-13, for a 1:1 electrolyte (KBr), at intermediate pH (pH = 7). Similar results were found for each latex with the pH not shown in these Figures. The linear relationship expected from Eq. (1) and required from the DLVO theory is confirmed in all cases, because the correlation coefficients were higher than 0.98, with at least seven experimental points. The ccc values were calculated and are shown in Table 2 for both

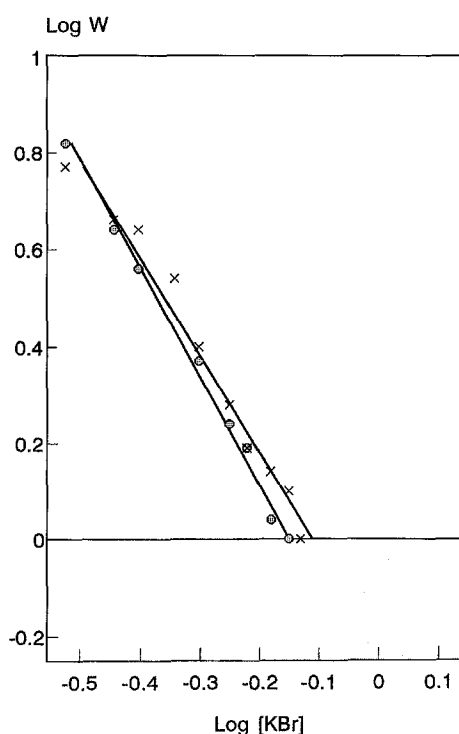


Fig. 1. Stability factor (W) versus KBr concentration for latexes SN-8 (●) and SN-13 (x), at pH = 7

Table 2. Critical coagulation concentration (ccc) of sulfonated latexes at different pH for 1:1 electrolyte (KBr)

	ccc (mM)			
	pH 3	pH 5	pH 7	pH 9
SN-8	560	763	715	710
SN-13	546	778	778	700

latexes and a pH range between 3 to 9. The first significant result is the high ccc value for sulfonated latexes, which confirms the previous expectations from their electrokinetic and surface characterizations [5–7]. This is especially noticeable because the sulfonated latexes are surfactant free and, in principle, the stabilization is only due to electrostatic repulsion. The ccc value of around 0.75 M, at intermediate pH, is higher than the physiological ionic strength (approximately 0.15 M) and, therefore, the sulfonated latexes could be potentially applicable in conditions where the monodispersity and colloidal stability are important, as in the development of immunoassays.

Table 2 also shows that the pH has a clear effect on the ccc when pH = 3, for both latexes, but for intermediate or basic pH there is not a clear trend. Each ccc value presented in Table 2 is the average of, at least, two measurements. The strong acid character of the sulfonate surface groups yields the independence of the colloid stability against the pH of the solution, when this is higher than 5, which is in agreement with the electrokinetic behavior shown by these latexes [5, 6].

In Table 2 the ccc values are relatively similar for both latexes, although slightly higher for the latex with a higher surface charge density, σ (SN-13), at least for intermediate pH. Previous reports, however, conflict with respect to the relationship between surface charge density and ccc [4, 9, 12–14]. Sometimes hardly any effect of surface charge density on the ccc was found [12, 14], however large effects were also observed [4, 9, 13]. Due to the differences found in the σ values for our latexes, the ccc of latex SN-13 should be significantly greater than that for SN-8. The ccc values, however, were not very sensitive to changes in the surface charge density and are similar, especially at extreme pH. The ccc values found at intermediate pH are the average of two

experiments, but we were not able to obtain a clear trend, probably due to the high electrolyte concentration that we had to use.

Considering the DLVO theory, Reerink and Overbeek [10] related the slope of the stability curve, $(d \log W / d \log C)$, to the particle radius a , the diffuse potential ψ , and the electrolyte valence z . This is given by:

$$-(d \log W / d \log C) = 2.15 \times 10^7 a \gamma^2 / z^2, \quad (2)$$

where

$$\gamma = [\exp(z e \psi / 2 k T) - 1] / [\exp(z e \psi / 2 k T) + 1]. \quad (3)$$

In Eq. (3) e and μ have their usual meaning, electron charge and Boltzmann constant. The Hamaker constant, which characterizes the attractive interaction between two particles, can be obtained experimentally from the slope of the stability curve and the ccc value of the latex [10, 15]. For a symmetrical electrolyte the Hamaker constant A , the ccc, the valence z , and γ can be related by the following equation [15]:

$$\text{ccc} = 3.6 \times 10^{-36} \gamma^4 / z^6 A^2, \quad (4)$$

where the ccc is in mol/l.

Using the ccc from Table 2 and the ζ -potential from electrokinetic measurements, we can calculate the Hamaker constant by Eq. (4). Previously, we have assumed the diffuse and zeta (ζ) potentials to be the same [15]. This is a good approximation at high ionic strength and particularly when this is as high as 0.7 M [7, 16]. We have estimated the ζ -potential of both latexes from electrophoretic mobility measurements. Figure 2 shows the ζ -potential versus the electrokinetic radius (κa), for 1:1 and 2:2 electrolytes. The ζ -potential values were obtained by the Dukhin and Semnikhin theory [7]. Due to the difficulties to measure the mobility at so high concentration (0.75 M), the ζ -potentials were obtained by extrapolation to the specific ccc values for the electrolyte 1:1. To check the ζ -potentials obtained by extrapolation, we have compared these values with the diffuse potentials calculated by Eq. (2), using the slopes from Fig. 1, at pH = 7: for latex SN-8, $\psi = 33$ mV and $\zeta = 38$ mV; and for latex SN-13, $\psi = 31$ mV and $\zeta = 31$ mV. Thus, both potentials are similar and the ζ -potential values found by extrapolation seem to be acceptable.

The A values are shown in Table 3 for both latexes and a monovalent electrolyte (KBr). The A value for each sulfonated latex is the average obtained from the results at pH 5, 7, and 9.

The theoretical value of the Hamaker constant for polystyrene/water system is 1.37×10^{-20} J [17]. Our experimental values are lower than this, especially for latex SN-13. However, the A value of latex SN-8 is similar to those obtained by several authors [18–21]. Although the A values experimentally found for polystyrene/water system can vary even one order of magnitude [4, 22]. Thus, the result for latex SN-8 seems to be in relatively good agreement with the theoretical A value and, therefore, the mechanism for the colloid stability would be mainly the electrostatic repulsion. Since the Hamaker constant is considered to be an intrinsic property of the bulk material, the A values should be the same for both latexes. Therefore, the latex SN-13 seems to have a steric contribution to its colloidal stability that would yield a high ccc and a lower ζ -potential [2, 6, 7]. Due to the method of preparation of our sulfonated latexes, we believe that a layer of water soluble polymers or oligomers exists on the surface of these particles [5, 6, 12]. That layer enhances the colloidal stability of our latexes and is thicker for latex SN-13, which was prepared with a greater amount of NaSS in the second injection (Table 1). These results are also in agreement with those obtained by Tamai et al. [12], who proposed a similar model for the electric double layer to explain the results with P(St/AA) and P(St/HEMA) latexes.

In order to check our previous finding, we have also studied the colloid stability of both sulfonated latexes in the presence of a symmetrical 2:2 electrolyte, $MgSO_4$. Figure 3 shows the experimental points of $\log W$ versus $\log C$ for latex SN-8 and SN-13, at pH = 3. With the 2:2 electrolyte the linear dependence was not as good as in Fig. 1, especially at pH = 9, although we have repeated

Table 3. Hamaker constant (A) of sulfonated latexes in the presence of 1:1 (KBr) and 2:2 ($MgSO_4$) electrolytes

	$A (10^{-20} J)$	
	KBr	$MgSO_4$
SN-8	0.88	0.41
SN-13	0.59	0.32

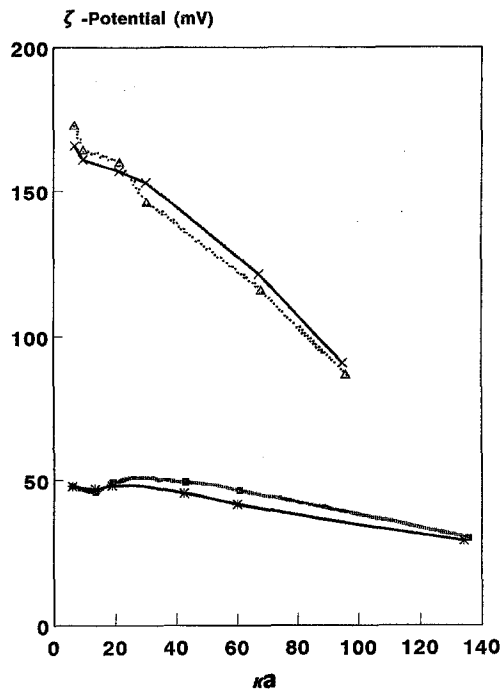


Fig. 2. ζ -potential versus electrokinetic radius (κa) for 1:1 and 2:2 electrolytes: KBr, SN-8 (\times) and SN-13 (\triangleright); $MgSO_4$, SN-8 ($*$) and SN-13 (\blacksquare).

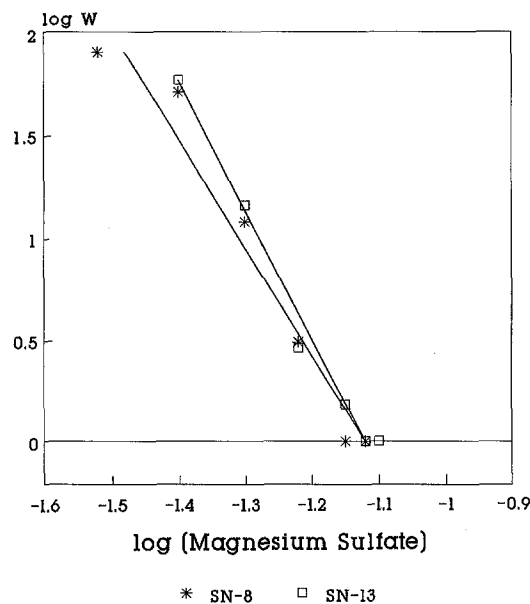


Fig. 3. Stability factor (W) versus $MgSO_4$ concentration for latexes SN-8 ($*$) and SN-13 (\square) at pH 3.

all the experiments several times. This is the reason why we have used Eq. (4) for determining the Hamaker constant, instead of Eq. (2) which includes the slope, ($d \log W / d \log C$).

The ccc values for both latexes at three pH values are shown in Table 4. Again there is not a clear difference between the latexes, although the latex with a higher σ (SN-13) displays a slightly higher ccc at pH 7. In the presence of $MgSO_4$ the ccc at pH 3 is equal to the ccc at pH 4.5, which means that under these conditions the concentration of the divalent electrolyte is more important than the effect of pH. But the most significant result in Table 4 is that, in all cases, the ccc values are nearly one order of magnitude lower than those obtained with KBr.

For large values of the diffuse potential, where γ approaches 1, Eq. (4) produces the Schulze-Hardy limit [23]:

$$ccc = K'/z^6 A^2 \quad (5)$$

For low values of ψ , where γ approaches $ze\psi/4kT$, one obtains the Debye-Huckel limit [23]:

$$ccc = K'(e\psi/4kT)^4 / z^2 A^2 \quad (6)$$

Thus, considering a constant value for A , the variation of ccc with z should be between the predictions of Eqs. (5) or (6) (the power of z between 6 and 2) and with the actual value depending upon the magnitude of ψ [4].

For our system, the ζ -potentials estimated in the presence of $MgSO_4$ are shown in Fig. 2. By measuring the electrophoretic mobility at a concentration similar to the ccc, the ζ -potential was -20 mV, independently of the theory used [7], and ζ can be considered in the intermediate range for the application of Eqs. (5) or (6). For a simple comparison, if we consider Eq. (5), the differences found for the ccc of a monovalent or a divalent electrolyte, would give rise to a power of z of 3.3, that can be considered intermediate between 2 or 6. This re-

sult is in agreement with those by Tsauro and Fitch [4], who found a power of z between 2.4 and 5.5.

Again we can calculate the Hamaker constant for sulfonated polystyrene latexes, by using Eq. (4) and the results from electrokinetic and ccc data for a 2:2 electrolyte. Table 3 also shows the average Hamaker constant values obtained for sulfonated latexes in the presence of a divalent electrolyte. The A value of latex SN-8 (with a lower σ) is the greater one, but both are now significantly lower than those calculated with a monovalent electrolyte; and, therefore, lower in comparison with the theoretical one. Again, a steric stabilization can be assumed in the same way as for a monovalent electrolyte. Due to the low A values, the steric contribution seems to be more significant for a divalent electrolyte. This is because even at low concentration of $MgSO_4$, the ζ -potentials are comparatively lower than with KBr [7], and the surface charge of the particle is more effectively screened, diminishing the electrostatic repulsion.

In conclusion, sulfonated polystyrene latexes are colloidally very stable even when they were prepared by surfactant free emulsion polymerization. By combination of electrokinetic and colloid stability data, the Hamaker constant can be estimated and compared with the theoretical one. The results of that comparison may give us more information about the colloidal stabilization mechanism of the latex particles. In the case of sulfonated polystyrene latexes, there is an important electrostatic contribution to the colloid stability due to the high surface charge density. But also there seems to appear a steric contribution due to the structure of the electric double layer which surrounds the particles, this contribution being more important for the latex with a higher electric charge on the surface.

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Table 4. Critical coagulation concentration (ccc) of sulfonated latexes at different pH for 2:2 electrolyte ($MgSO_4$)

	ccc (mM)		
	pH 3	pH 4.5	pH 7
SN-8	75	73	78
SN-13	75	75	83

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